



Integrated copper-containing wastewater treatment using xanthate process

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Abstract

Although, the xanthate process has been shown to be an effective method for heavy metal removal from contaminated water, a heavy metal contaminated residual sludge is produced by the treatment process and the metal-xanthate sludge must be handled in accordance with the Taiwan EPA's waste disposal requirements. This work employed potassium ethyl xanthate (KEX) to remove copper ions from wastewater. The toxicity characteristic leaching procedure (TCLP) and semi-dynamic leaching test (SDLT) were used to determine the leaching potential and stability characteristics of the residual copper xanthate (Cu-EX) complexes.

Results from metal removal experiments showed that KEX was suitable for the treatment of copper-containing wastewater over a wide copper concentration range (50, 100, 500, and 1000 mg/l) to the level that meets the Taiwan EPA's effluent regulations (3 mg/l). The TCLP results of the residual Cu-EX complexes could meet the current regulations and thus the Cu-EX complexes could be treated as a non-hazardous material. Besides, the results of SDLT indicated that the complexes exhibited an excellent performance for stabilizing metals under acidic conditions, even slight chemical changes of the complexes occurred during extraction. The xanthate process, mixing KEX with copper-bearing solution to form Cu-EX precipitates, offered a comprehensive strategy for solving both copper-containing wastewater problems and subsequent sludge disposal requirements. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Xanthate process; Copper removal; Semi-dynamic leaching test; Leaching toxicity; Stability characteristics

Abbreviations: FTIR, Fourier-transform infrared; KEX, potassium ethyl xanthate; ORP, oxidation–reduction potential; SDLT, semi-dynamic leaching test; Taiwan EPA, Taiwan environmental protection administration; TCLP, toxicity characteristic leaching procedure; XPS, X-ray photoelectron spectroscopy

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1. Introduction

Heavy metal contamination exists in the aqueous waste streams of many industries, and these wastewaters, with a high concentration of heavy metals are difficult to remove and dispose. Current methods for the removal and recovery of heavy metals from wastewaters include chemical treatment with lime, the use of caustic materials, ion exchange, adsorption, reverse osmosis, membrane filtration and precipitation [1,2]. The precipitation process is most widely used of the treatment process [3]. However, traditional precipitation process by formation of a metal hydroxide cannot always yield a satisfactory metal removal efficiency. Furthermore, metallic ion precipitation usually produces large amounts of sludge, which may leach metals subsequently. Consequently, this sludge needs further treatment such as solidification.

The cement-based solidification/stabilization (S/S) process can effectively treat various hazardous wastes, such as metal-bearing sludges, for safe disposed in landfills [4]. The alkalinity existing in the cement-based paste affords a high pH environment and confines metal mobility to solidified matrices. However, recent investigations of the long-term stability of S/S-treated wastes indicate that the high concentration of acidic leachants leach a large amount of metals in the leaching zone [5–7]. The alkalinity of the cement-treated matrices is vulnerable in an acidic environment.

A xanthate process was recently used for precipitation/stabilization of metals [8,9]. Xanthates are a family of compounds prepared by mixing alcohol with potassium hydroxide and carbon disulfide. Similar to the reactions between sodium sulfide and heavy metals, the xanthates reacted with metals to form metal-xanthate complexes. Owing to the low solubility products and high stability constants of metal-xanthate complexes, the xanthate process had been claimed to have a high removal efficiency for heavy metals in wastewater [10–12]. The xanthate process produces less sludge than hydroxide precipitation combined with cement solidification. Furthermore, xanthate process was found to be preferable to sulfide precipitation since there is no problem with residual sulfide in the treated wastewater.

Although, several researches have studied the metal removal efficiency of wastewater using xanthate [8–12], it should be noted that the final disposal of the precipitated metal-xanthate complexes is still of concern. The sludge before it can be safely disposed in landfills must meet current waste disposal requirements. However, few studies have focused on this issue. The purpose of this research was to solve both copper ion removal from wastewater and subsequent copper xanthate (Cu-EX) sludge disposal using xanthate processes. The metal removal research was performed to explain how xanthate effectively removes copper ions from solution. The toxicity characteristics leaching procedures (TCLP) was used as a pass/fail test to evaluate the leaching toxicity of the Cu-EX complexes (sludge). Additionally, the semi-dynamic leaching test (SDLT) was utilized to investigate the metal leachability and stability characteristics of the Cu-EX complexes when they are immersed in an acidic disposal environment. The use of UV-visible spectra and X-ray photoelectron spectroscopy (XPS) analyses are also used to gain a fundamental understanding of the complex's chemical changes during SDLT.

2. Materials and methods

2.1. Preparation of potassium ethyl xanthate

All chemicals used were analytical grade quality. Deionized water was used in all experiments. The potassium ethyl xanthate (KEX, $C_2H_5OCS_2K$), was used as a metal chelating agent and prepared according to Vogel and Furniss' method [13], namely by the reaction of sodium hydroxide containing ethyl alcohol (NaOH added to excess ethyl alcohol) with CS_2 at $10^\circ C$. The product was purified by three times of dissolution in acetone and recrystallization with petroleum ether [10]. The resultant material was then filtered, washed with ether, vacuum dried, and stored in a dessicator. The chemical structure of the xanthate was identified using X-ray diffraction and elemental analysis.

2.2. Metal removal studies and copper xanthate complex formation

The xanthate process, interacting aqueous solutions containing KEX and a synthetic wastewater containing $Cu(NO_3)_2$, was tested at four different copper concentrations (50, 100, 500, and 1000 mg/l) to evaluate the metal removal ability of xanthate. During the xanthate treatment process, a KEX solution was dosed with a KEX/copper molar ratio of 2, as suggested by Rao [10], to form a stoichiometric mixture of a Cu-EX complex. Gentle agitation was applied during the 30 min contacting period at room temperature. The brown Cu-EX complex was then filtered through a $0.45 \mu m$ membrane paper, thoroughly vacuum dried and stored in a dessicator. The resultant Cu-EX complexes were identified by use of X-ray diffraction and Fourier transform infrared (FTIR) analyses. The Cu-EX complexes formed from a 1000 mg/l copper solution with related KEX solution was used in subsequent TCLP and SDLT experiments. The filtrate analyzed for copper using atomic absorption spectroscopy (Perkin-Elmer 5100) to evaluate the copper removal efficiency of the xanthate process.

2.3. Toxicity evaluation—toxicity characteristics leaching procedure(TCLP)

The TCLP [14] has been recognized as a leading test for evaluating the leaching toxicity potential of materials. Herein, the TCLP involved the agitation of a ground and pulverized Cu-EX complex ($<9.5 \text{ mm}$) in a leachate using a leachant/waste ratio of 20. The extraction (at $22 \pm 3^\circ C$) was achieved by tumbling the specimens for 18 h, after which the samples were separated into solid and liquid phases by filtering through a $0.7 \mu m$ borosilicate glassfiber filter. The resultant TCLP leachate (filtrate) was analyzed for heavy metals using atomic absorption to determine the degree of elution of components from the solid specimens.

2.4. Copper leachability and stability characteristics of copper xanthate complex

A series of SDLT was performed to examine the copper leachability and stability characteristics of the Cu-EX complex. A 1N acetic acid solution was used as the leachant to simulate the complex disposed in an acidic environment. During SDLT, a solution-to-solid

ratio of 20 (200 ml leachant/10 g dry Cu-EX complex) was used and repeated extractions were conducted by refreshing leachant at 1-day intervals with a total of 60 times replacement. The sample in the extraction bottle was separated into liquid and solid phases by filtering through 0.45 μm membrane papers.

The leached copper and xanthate species in the liquid phase samples were examined using an atomic absorption spectrometry and an UV-visible spectroscopy (Shimadzu UV-1201 spectrophotometer). Solid phase samples were freeze dried, ground and pulverized to fine powders. Then XPS (VG ESCA 210 system) of the solid phase sample was carried out to determine the oxidation state of copper of the Cu-EX complexes.

3. Results and discussion

3.1. Characterization of KEX

The comparisons of elemental and X-ray diffraction analyses results of the synthetic and commercial (Tokyo Kasei, Japan) KEX are given in Table 1 and Fig. 1. The synthetic KEX exhibited similar chemical compositions (C, H, and S) with the commercial product. Also, the results of the X-ray diffraction analyses revealed similar patterns of synthetic and commercial KEX. The FTIR spectra further displayed the same pattern of both synthetic

Table 1
Elemental analysis of potassium ethyl xanthate (KEX)

	Element (% by mass)		
	C	S	H
KEX commercial	21.9	36.0	3.2
KEX synthetic	22.5	38.1	3.1

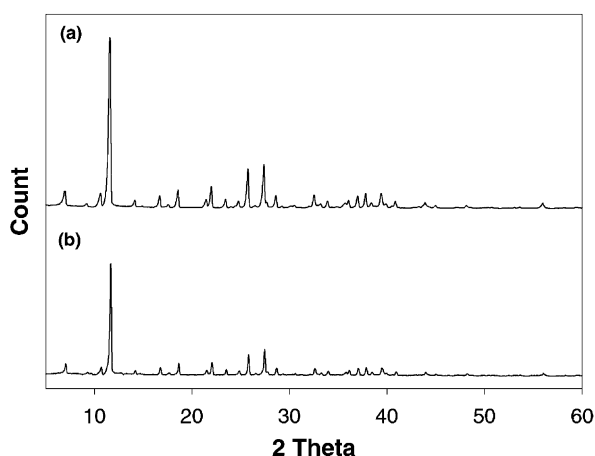


Fig. 1. X-ray diffraction patterns of potassium ethyl xanthate, (a) commercial and (b) synthetic.

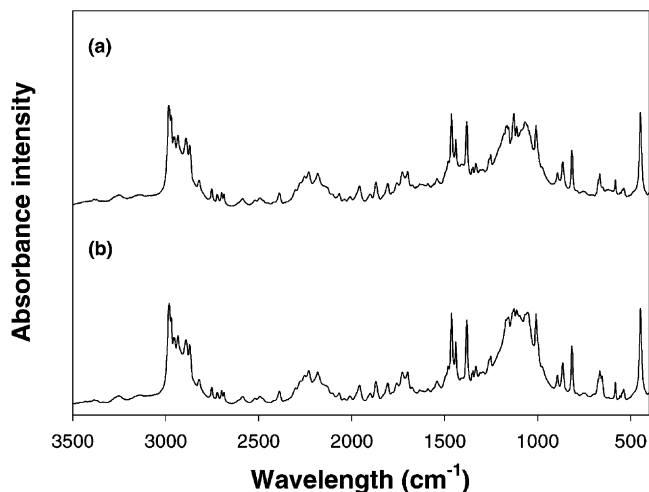


Fig. 2. FTIR spectra of potassium ethyl xanthate, (a) commercial and (b) synthetic.

and commercial KEX (Fig. 2). These measurements essentially confirmed a KEX structure of the synthetic compound.

3.2. Copper removal in the presence of KEX

Table 2 contains the results of the degree of copper removal by the xanthate process at four different copper concentrations (50, 100, 500, and 1000 mg/l) with a KEX/copper molar ratio of 2. As the results shown, the residual copper concentrations in the solutions after the xanthate treatment all were below detection limits (<0.077 mg/l). The results show that the xanthate process was effective for the precipitation of copper-containing wastewater with a wide copper concentration range, and the treated wastewater could meet the effluent standard (3 mg/l) of Taiwan EPA's regulations [15].

Figs. 3 and 4 showed the XRD patterns and FTIR spectra of Cu-EX complexes formed at the four copper concentrations with KEX as mentioned above. The qualitative XRD patterns (Fig. 3) of the four Cu-EX complexes displayed the same crystalline data. Also, the four Cu-EX complexes exhibited the same FTIR spectra (Fig. 4). As a result, the copper concentration of the wastewater would not affect the performance of the xanthate process.

Table 2
Experimental results of copper removal program

	Initial copper concentration (mg/l), before mixing			
	1000	500	100	50
Residual copper (mg/l)	ND	ND	ND	ND
Copper removal (%)	100	100	100	100
Ionic strength (I)	0.03938	0.01969	0.00394	0.00197

ND: indicates not detected under detection limits of 0.077 mg/l.

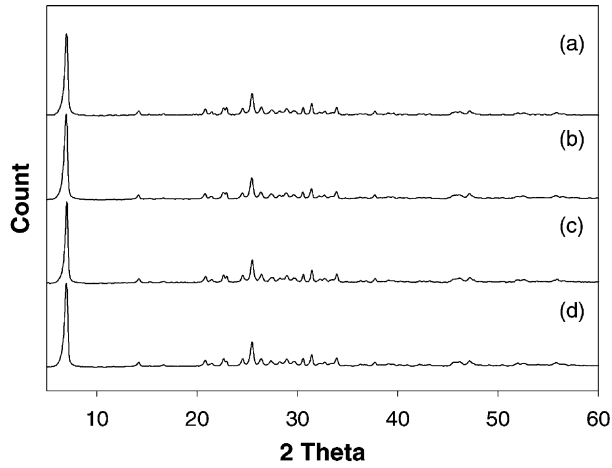


Fig. 3. X-ray diffraction patterns of Cu-EX complex. Initial Cu(II) concentration: (a) 50 mg/l, (b) 100 mg/l, (c) 500 mg/l, and (d) 1000 mg/l.

Considering the required amount of Cu-EX complexes for following TCLP and SDLT, the complex produced by using 1000 mg/l copper solution with related KEX solution was used for further experiments.

3.3. TCLP results

The results of TCLP herein showed that no copper ion was detected in the TCLP leachate of the Cu-EX complex. The leached copper concentration was much lower than Taiwan

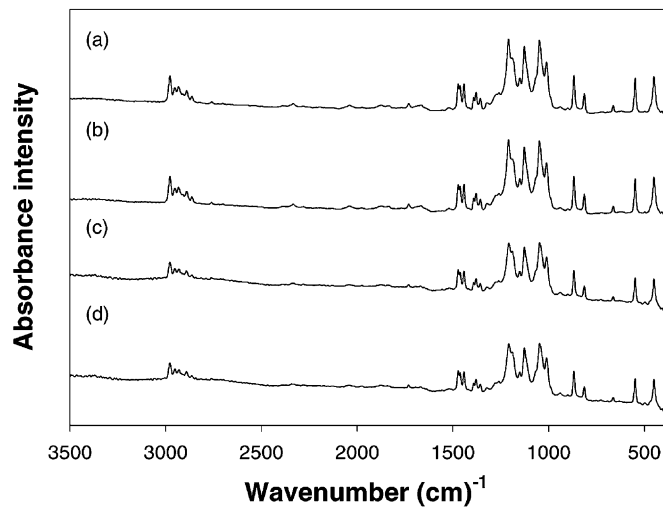


Fig. 4. FTIR spectra of Cu-EX complex. Initial Cu(II) concentration: (a) 50 mg/l, (b) 100 mg/l, (c) 500 mg/l, and (d) 1000 mg/l.

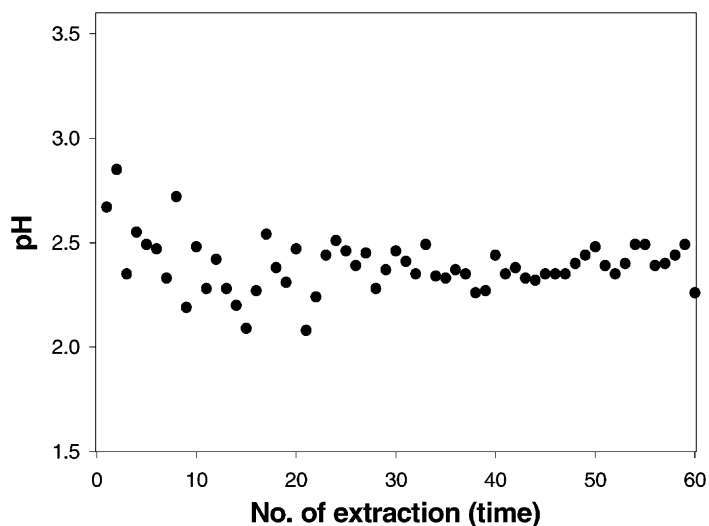


Fig. 5. Changes in pH value of filtrate at various intervals of semi-dynamic leaching test.

EPA's TCLP regulatory limits (15 mg/l). Consequently, it was reasonable to conclude that Cu-EX complex was not a leaching-toxic and could be classified as a non-hazardous waste, which could be disposed off in sanitary landfills without further treatment.

3.4. Stability characteristics and leaching behavior of Cu-EX complex

In addition to the TCLP test, a series of SDLT using 1N acetic acid solution as leachant were conducted to examine the copper leachability and stability characteristics of the Cu-EX complex in simulated acidic landfill environments. Fig. 5 reports the pH value of the filtrate for each extraction run during SDLT. The pH values were within the range of 2–3, illustrating that the filtrates were well buffered by the acetic acid solution. Fig. 6 contains the results of copper released from the Cu-EX complex during SDLT. At the initial stage of SDLT, copper ion was not found in the filtrate; however, small amounts of copper were released from the Cu-EX complex with progressive leaching over a 30-day extraction period. This phenomenon implied that Cu-EX complex might undergo chemical changes after continuous acetic acid extraction. The oxidation–reduction potential (ORP) values of filtrates (Fig. 7) also displayed a significant change after a 30-day extraction period. A rising trend from 0 to 250 mV indicated that reductive materials were diminished in the process of SDLT.

The accumulative amount of leached copper by SDLT (Fig. 6), showed that the total amount of leached copper was only 0.82% of the initial amount. The results indicated that the Cu-EX complex would not cause the threat of instantly releasing metal under acidic conditions. Lin [7] conducted a similar SDLT leaching process for the investigation of the dicalcium silicate and copper oxide S/S system. From his research, the accumulated fraction of leached copper by SDLT was determined to be as high as 75% of the copper oxide /dicalcium silicate solidified matrix after 60-day's extractions. In comparison of the

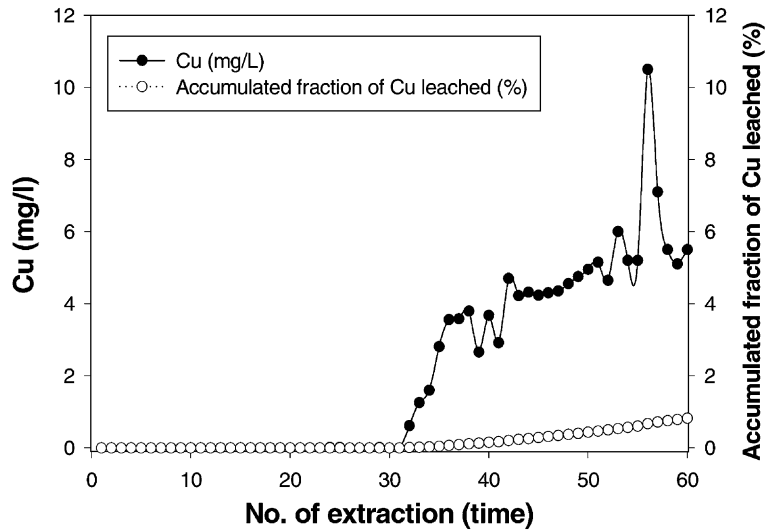


Fig. 6. Copper ions and accumulated fraction of copper released from Cu-EX complex at various intervals of semi-dynamic leaching test.

SDLT results of the xanthate and S/S process, it revealed that Cu-EX complex had a better copper stabilizing efficacy than the solidified matrix in 1N acetic acid solution.

Although, the Cu-EX complex passed the TCLP and exhibited good copper stabilizing efficacy in SDLT, it is essential to understand the stabilization mechanism and chemical

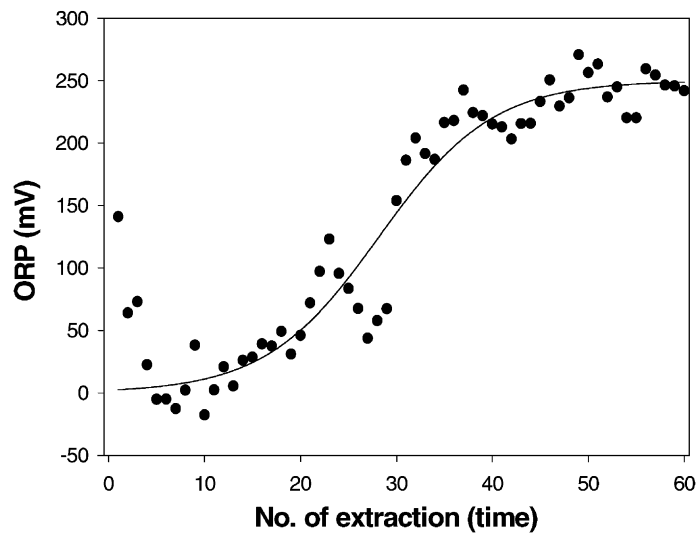


Fig. 7. Changes in ORP value of filtrate at various intervals of semi-dynamic leaching test.

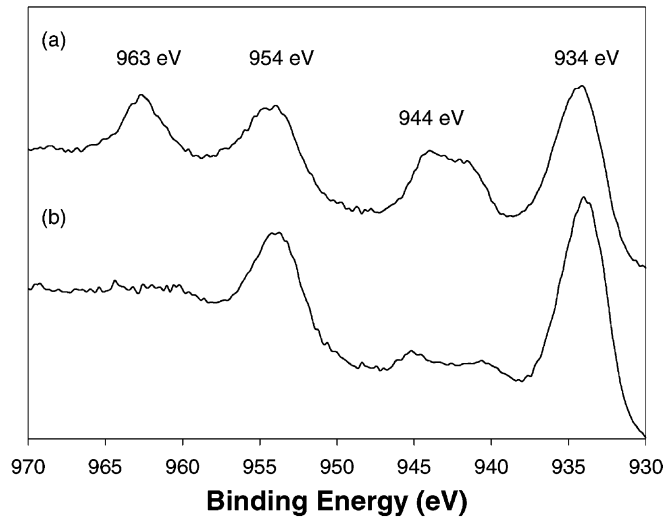
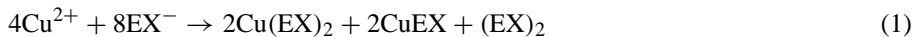


Fig. 8. X-ray photoelectron spectra of Cu-EX complex, (a) before and (b) after 60-day periods of semi-dynamic leaching test.

changes of the Cu-EX complex during SDLT. The XPS analyses of Cu-EX complexes before and after SDLT were carried out to examine the change of oxidation state of copper in the Cu-EX complexes. Fig. 8 shows the XPS spectra. As shown in the Fig. 8(a), the major peaks in the XPS spectrum of Cu-EX complex before SDLT appeared at binding energy of 963, 954, 944, and 934 eV. The component at binding energy of 944 and 963 eV is the cupric xanthate signal, while the signals at binding energy of 934 and 954 eV are due to the cuprous xanthate [16,17]. From the XPS analysis, one concludes that the Cu-EX complex formed by the xanthate process should contain both cuprous and cupric form species. The formation of Cu-EX complex is, therefore, expressed as below:



where EX^{-} , $\text{Cu}(\text{EX})_2$, CuEX , and $(\text{EX})_2$ are relative to xanthate ion, cupric xanthate, cuprous xanthate, and dixanthogen ($\text{C}_2\text{H}_5\text{OCS}_2$)₂, respectively. Similar studies by Sheikh and Leja [16] demonstrated that both cupric xanthate and cuprous xanthate were found when the complexes were formed by the xanthate process for the removal of copper ion from aqueous system. In the meantime, both the reduction of the cupric xanthate and the oxidation of xanthate ion would form cuprous xanthate and dixanthogen.

After 60-day SDLT extractions, only two major peaks at 954 and 934 eV occurred in the XPS spectrum of the Cu-EX complex (Fig. 8(b)). The absence of cupric xanthate (with the absence of satellite structure at binding energy of 944 and 963 eV in the Fig. 8(b)) indicated that cuprous xanthate to be the more stable species in the Cu-EX complex (Fig. 8(b)). The reaction involved is:



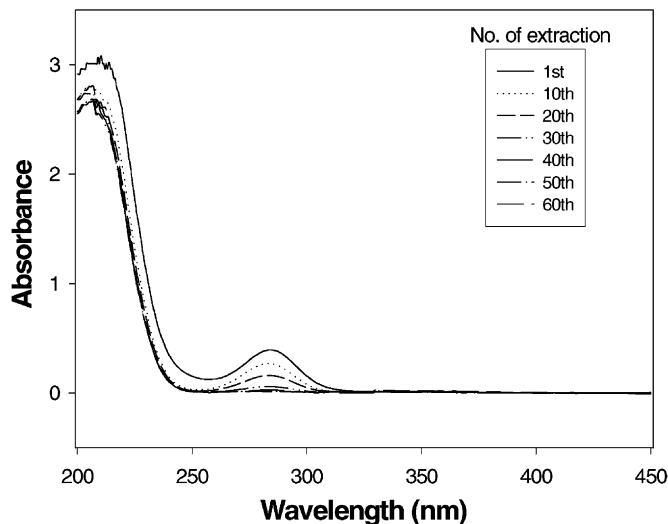
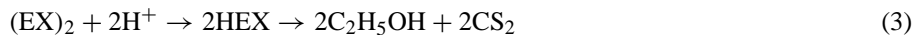


Fig. 9. UV-visible spectra of filtrate (diluted with ten times) at various intervals of semi-dynamic leaching test.

The decomposition of Cu-EX complex during SDLT at various time intervals was examined by monitoring dixanthogen $(EX)_2$ and carbon disulfide (CS_2) in the filtrates with an UV-visible spectroscopy. Fig. 9 shows the UV-visible spectra of the SDLT filtrates at various time intervals. Two absorption bands, 283 and 206 nm, were found in the UV-visible spectra of the filtrates obtained at the beginning of SDLT. The absorption band at 283 nm is attributed to $(EX)_2$, while that at 206 nm is attributed to CS_2 , as demonstrated by Sparrow et al. [18] and Leja [19]. During the SDLT extraction, both absorption intensities of $(EX)_2$ and CS_2 decreased with increasing extraction time. And at the end of SDLT, the CS_2 was the only species found in the spectra. That result was reasonable since $(EX)_2$ may decompose to yield CS_2 [20,21], and CS_2 was produced immediately especially at low pH conditions [10,16,18,20,21]:



Since CS_2 is the final product of the decomposition of $(EX)_2$, the decreasing trend of CS_2 in Fig. 9 revealed that less $(EX)_2$ was decomposed from the Cu-EX complex as SDLT extraction time increased. The decline of $(EX)_2$ in the filtrate was due to the complete change of cupric xanthate to cuprous xanthate, according to Eq. (2). Consequently, these results confirmed again that the cuprous xanthate should be the major stabilizing structure of the Cu-EX complex in acidic environment.

4. Conclusions

The xanthate process can effectively treat wastewaters with a wide range of copper concentrations to a level that meets current effluent limits. The Cu-EX complex formed in

the metal removal program can also meet the TCLP regulations, indicating the complex to be a non-hazardous material. Therefore, the sludge produced by xanthate process could be directly disposed off in sanitary landfills without further treatment. Furthermore, results of the SDLT showed that the total amount of leached copper was only 0.82% of the initial Cu-EX complex; and cuprous xanthate was the major stabilizing structure, which was unaffected by SDLT. From the above results, it was concluded that xanthate process could be an effective technic for solving copper-containing wastewater and subsequent sludge disposal problems, which differ from the traditional hydroxide precipitation treatment combined with cement solidification process.

Acknowledgements

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